International Journal of Geospatial and Environmental Research

Volume 7
Number 2 *AAG West Lakes Division Meeting 2019*

Article 4

October 2020

Scale Mis-Matches When Assessing Chloride Concentration and Corrosiveness Using Statewide Data for Trend Analysis

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Abstract

This study compares chloride concentrations and a series of corrosiveness indexes to determine whether trends in statewide databases appropriately detect local conditions. Chloride concentrations in local, urban streams generally persist at higher levels than what is typical of natural waters. Data collected for statewide water quality assessments are often at a broader geographical scale. Results and subsequent policies may indicate little to no environmental concern, meanwhile degradation at the local scale remains relatively undetected. Pulses of local snowmelt runoff may violate water quality criteria, but long-term trends measured at the statewide scale are in decline. Results highlight the need for data at varying scales when assessing freshwater salinization and subsequent effects in urban watersheds.

Keywords

Chloride, Water Quality, Freshwater Salinization, Trend Analysis, Corrosiveness

Acknowledgements

Acknowledgements to Dr. Jerald Schnoor for his contribution to this work.

1 INTRODUCTION

Just as lack of testing can underestimate impacts of a pandemic, a lack of environmental monitoring data can give a false impression of ongoing conditions. Paucity and improper scales of measurement can lead to fundamental mismatches between the "story" data convey and actual conditions. Policy decisions stemming from such distorted evidence can lead to or perpetuate irreversible environmental damage. This paper demonstrates such phenomenon regarding issues of freshwater salinization and subsequent changes to water chemistry and suggests corrosiveness indexes as an assessment tool. Results determine the capacity for statewide water quality data from Iowa to assess corrosiveness using ten-year sample data, index calculations and statistical trend analysis. Conditions conveyed by statewide data give an incomplete, if not false impression that freshwater salinization is not occurring due to data paucity, the need for surrogate data in lieu of direct measurements, and a decline in long-term data collection sites. This paper considers the following research questions:

- What are long-term trends in chloride, metal concentrations and corrosiveness indexes for statewide water quality in Iowa?
- Do trends in freshwater salinization indicate potential for corrosiveness?
- Do trends vary by land use?

Globally, freshwater systems are becoming saline as a result of human activity (Kaushal et al. 2014; Kaushal et al. 2005; Kaushal et al. 2018a). Because data adequate for assessing local conditions seldom exist, public statewide datasets often serve as a primary resource for environmental decision-making. But broad-scale, long-term measurements for soluble ions like chloride likely under-estimate the overall environmental impact. Initial research attempted to understand such environmental problems broadly, but locally-applied solutions may require refinement (Borgström et al. 2006). Complexity, interconnectedness and dynamic characteristics of ecological systems become generalized and over-simplified when assessing a larger spatial or temporal scale. The result may lead to Type II errors where no evidence of freshwater salinization concern actually masks acute and chronic water quality violations at the local scale. Policies are based on inaccurate measurements, meanwhile freshwater salinization abounds, and subsequent environmental degradation remains relatively undetected.

1.1 Freshwater Salinization Trends

National-scale trend analysis by the US Geological Survey (USGS) and the National Academies of Sciences emphasize the need for more localized understanding of freshwater salinization over time and space (Kaushal et al. 2005; Kaushal et al. 2018a). Evidence may come in the form of detecting general chloride trends or also indicators of corrosiveness in water supply (Belitz et al. 2016; Kaushal et al. 2005; Stets et al. 2017). In both instances, positive trends suggest salinization occurs, and is increasing, at a faster rate in urban areas. The primary effect of more salt in fresh water is salinization itself: the water becomes saline. Secondary effects include systematic changes to water chemistry and other soluble materials, including metals from roadway surfaces. Such methods may provide unique evidence of primary and secondary effects of freshwater salinization not previously detected for the State of Iowa. However, results may grossly under-estimate conditions at the local scale.

Often researchers from professional water monitoring agencies rely on continuous and real-time primary data to generate national scales results from measurements taken on large river systems (Hirsch et al. 1982, 2010). Data are often collected from gauging stations equipped with sensors, sampling devices and other specialized data collection tools. City, county or quasi-governmental public works agency budgets suggest simpler tools and or methods to conduct similar studies. This complicates data collection at the local scale and limits the ability to use complex models which rely on such data. Efforts to reduce bias among monthly, annual and semi-annual regression analysis has occurred, but analysis still relies exclusively on data sets not typically available at the local scale (Hirsch 2014).

Comparing spatio-temporal trends to local data elucidates such scale mismatches. Nationwide trend analysis tends to concentrate on conditions in select, major water bodies (Smith 1990; Smith et al. 1997; Green et al. 2014). Even in the case of regional-scale analysis, local conditions can still remain undetectable (Barbosa et al. 2012; Viglione et al. 2013). Local data likely originate from field-based observations in small, ungauged streams. The flashy hydrology of urban streams often demonstrate extreme fluxes in concentration result in skewed data frequencies (Bannerman et al. 1993). Rather than compare data using mean values, medians often serve as a more appropriate measure of central tendency for such nonnormal data distributions (Hirsch and Slack 1984). Such small, often incomplete datasets render results of parametric statistical analysis unreliable.

Water quality data collected over a time series vary seasonally and typically follow serial correlation. This further violates parametric assumptions of independent subsequent measurements (Cohn et al. 1989; Cohn 2005; Helsel and Hirsch 1992). The Kendall-Theil robust line, or Sen's Slope Estimator (SSE) provides a nonparametric alternative to parametric methods for statistical analysis of water resources data (Helsel and Hirsch 1992). Theil–Sen slopes can be used to characterize average rates of change in specific conductance, pH, and base cation concentrations per year. The Theil–Sen regression estimates the slope of change in a parameter across time by calculating the median slope of all pairwise points in a series of hydrologic data at the local or regional scale with insensitivity to outlier values (Cooper et al. 2014; Stets et al. 2017).

1.2 Secondary Effects of Salinization

Persistent salt ions in solution at higher concentrations are only part of the problem. More recently, research has indicated secondary effects and resulting "chemical cocktails" require further investigation (Kaushal, et al. 2018b; Pieper et al. 2018). For example, as corrosiveness increases, calcite is more likely to dissolve in a solution. The result is likely an even greater imbalance in cation/ion ratios and disproportional chemical balance of other dissolved ions in water. An ion imbalance such as this also alters pH and limits sequestration of other pollutants via deposition. Limestone or karst geology may reduce corrosion potential due to high concentrations of dissolved calcium. These carbonates sequester other mobile ions present, usually a function of groundwater activity. The result is usually evident in the form of lime scale where freshwater has contact with either soil, pipes, or another solid surface.

Surface runoff differs chemically from groundwater. Lime scale occurs when carbonate ions are present, such as in groundwater. However, surface water hydrology tends to dominate urban runoff, with little to no carbonate ions in dilution (Delleur 2003). Increased flow regimes can dilute the concentration of dissolved ions in surface water.

Indexes used by the water supply industry can determine the potential for untreated water to corrode distribution networks (Langelier 1936; Larson et al. 1942; Edwards and Triantafyllidou 2007). However, these indexes have not been generally applied to ambient surface water data to assess conditions.

1.3 Effects of Urbanization and Salt for Winter Road Maintenance

The United States mines approximately 36 million metric tons of rock salt a year, half of which is spread on paved surfaces to make winter roads safer for people and vehicles (Jackson and Jobbágy 2005). This is 100 times the volume of salt applied in the 1940s when the material was introduced as a winter road maintenance activity. As cities grow in cold-climate regions, more salt is mined and applied. Nationwide trends have been measured at broad scales, with general conclusions based on data from large, major river systems (Kaushal et al. 2005). If trends in chloride concentration align with increased urbanization, surface waters in population centers such as the northeastern United States will be rendered saline, non-potable for human consumption and toxic to freshwater organisms within the next century: the question is a matter of where, when, and *to what extent* (Cañedo-Argüelles et al. 2013).

As population centers, urban environments present even more complex, unique challenges to water resources management. The most interesting and compelling problems in the water resources field are multifaceted and multidisciplinary in nature, often highly so (Stephens et al. 2012). Urban water quality only grows in complexity as cities expand. Impervious surfaces and heterogeneous land cover generate runoff that requires efficient drainage or infiltration for volume reduction and pollutant removal. Climate, hydrology, geophysical characteristics and human intervention result in both the ecological services provided by water resources and the policies by which communities abide to maintain quality and quantity at multiple scales (Barbosa et al, 2012). Ungauged urban water bodies are potentially inaccurately assessed due to the general, landscape-scale of existing metrics (Castiglioni et al. 2009). Management decisions occur at the local level, based on data likely collected at a broader scale (Dennis et al. 2016). As a result, rapid temporal effects and acute loading of specific pollutants are likely under-estimated and improperly managed. This study provides insight to local inquiry of physical and human geographic systems to address these growing challenges.

Freshwater salinization is a growing global environmental concern, particularly as urbanization expands. As cities grow, so does the need to maintain transportation systems for human safety. In cold climate regions, the potential for permanent ecological damage also increases. Soils become less stable, and freshwater becomes saline (Norrström and Jacks 1998; Ramakrishna and Viraraghavan 2005; Robinson et al. 2017). Material typically bound to sediment such as nutrients and metals can mobilize in saline conditions, posing additional threats to water quality. As a conservative ion, the ultimate depository of all salts remains either in the water or soil. Concentrations accumulate over time and may be irreversible. The results of this study advance the capacity to rapidly, locally understand the ever-increasing effects of freshwater salinization.

A recent case study indicates variability in chloride concentrations based on location as well as local conditions (Kauten 2020). Chloride concentrations at the local scale appear to violate both acute and chronic water quality criteria. Meanwhile, statewide databases indicate a decrease in overall concentration over a ten-year period, as demonstrated by this study. In general, carbonate geology comprises a majority of

Iowa's physiographic regions (Prior 1991). Improved drainage of the Midwestern landscape since the 1940s has resulted in increased base flows for major river systems (Schilling et al. 2012; Zhang and Schilling 2006; Schilling and Helmers 2008). The agricultural landscape of Iowa also influences sediment concentrations in streams, which also impacts the ion balance of rivers and streams (Walling 1983; Streeter et al. 2018). While studies have investigated impacts of changes in ion concentrations linking groundwater and surface water, corrosiveness indexes have yet to be incorporated as a means of inquiry (Jin et al. 2019). The combination of increased base flow, sediment concentration and a lack of knowledge of surface water corrosiveness result in an incomplete assessment of freshwater salinization in Iowa waters, which ultimately may not be detectable at a coarse scale of measurement such as statewide monitoring data. Inconsistencies in measurements over time and spatial scales can fundamentally overlook a potentially growing concern for freshwater streams in cold climate regions.

2 STUDY AREA AND DATA

This study analyzed long-term datasets from the State of Iowa. The National Water Quality Exchange (WQX) database and the Iowa Department of Natural Resources (DNR) AQuIA databases provided an initial total of 7,992 sites where sample data exist, with 249 sites providing USGS data, and 7,741 locations for monthly data collected as part of the Iowa DNR Ambient Monitoring Program (ambient data) over the 2001-2010 and 2016-2018 time series.

Chloride, sulfate, metals, total alkalinity, total hardness (as CaMg), water temperature, and discharge as flow were selected for analysis. Because results were not available in the database at all statewide monitoring locations, locations where a minimum of 100 chloride samples existed from 2001 to 2010 were included. The time span was chosen due the database including records for more sites near cities sampled as part of the Iowa DNR Ambient Monitoring Program. After 2010, upstream and downstream sampling locations near many Iowa cities were eliminated from the Iowa DNR Ambient Monitoring Program sampling regimen and data are no longer collected for the sites (Iowa DNR (Department of Natural Resources) 2019).

Sites within a five-mile (8.05 km) radius of specific urban communities were categorized as rural locations, with the remaining sites classified as rural. The distance was estimated based on methods applied by Yin et al (2005). The cities selected are regulated under Clean Water Act requirements for municipal separate storm sewer (MS4) permits to manage for water quality protection (Chapman and Neprash 2005). This distance was chosen due to the potential for future development in the area, creating an opportunity to compare water quality and land use change over time in a community already regulated for water quality and watershed management. The area surrounding existing MS4 cities will likely experience future land use change in the form of more urban development, higher traffic concentrations, and proportionally higher impervious surface coverage beyond what other sites in Iowa will experience.

Mean chloride concentrations for all locations provide an initial comparative baseline to determine further research objectives. **Error! Reference source not found.**(A) contains 37 sites categorized as "rural," with green circles representing average chloride concentrations ranging from 21-34 mg/L, and orange triangles indicating locations where average chloride concentrations range from 7-21 mg/L, which is considered below normal conditions. Six sites located within five miles of an MS4

community in Iowa are included in Figure 1(B), with similar icons as the rural site locations. Average concentrations for these sites range from 15-43 mg/L. A red square represents average chloride ranges from 34-43 mg/L which are beyond what is considered "typical" chloride concentrations for Iowa waters by Iowa DNR (McDaniel 2009).

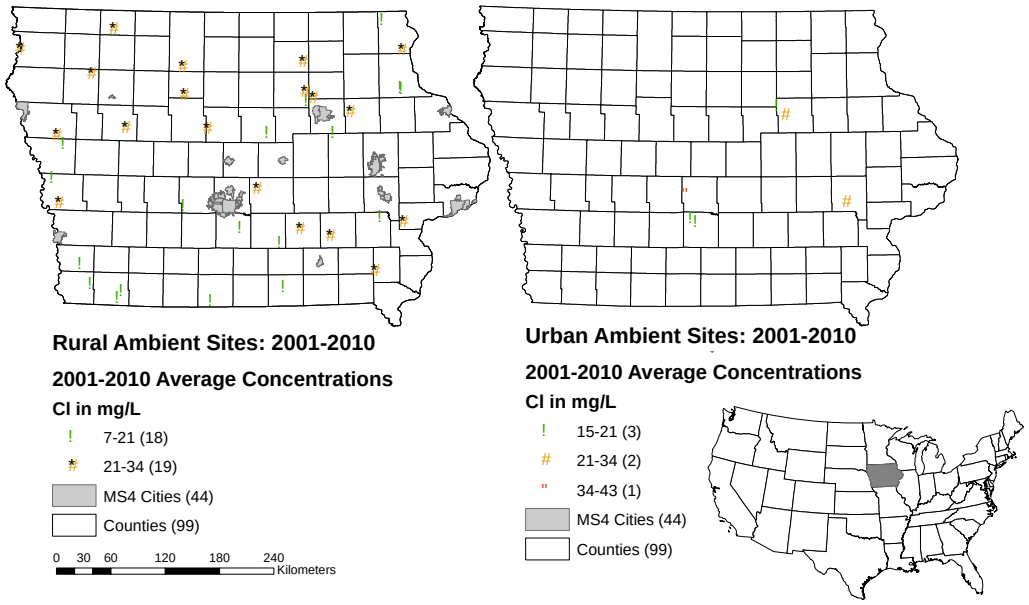

Figure 1. Average rural and urban chloride concentrations for study sites.

The total, final data set consisted of 37 rural locations and six urban locations. Figure 2 displays sites included in the study by urban and rural classifications, along with the location of MS4 cities located in Iowa. Site selection was reduced to the date range of January 1, 2001 to December 31, 2010 to account for the time span where sites in proximity to urban areas were available. Data were further reduced to locations with no fewer than 100 total chloride measurements per site. A total of 43 sites were selected based on these criteria. Microsoft® Excel was used to calculate median concentrations for chloride, and parameters used to calculate corrosiveness indexes. The table was joined with existing mean and maximum values generated by ArcMap 10.6.2. Median and maximum concentrations were used to calculate subsequent statistics and trend analyses.

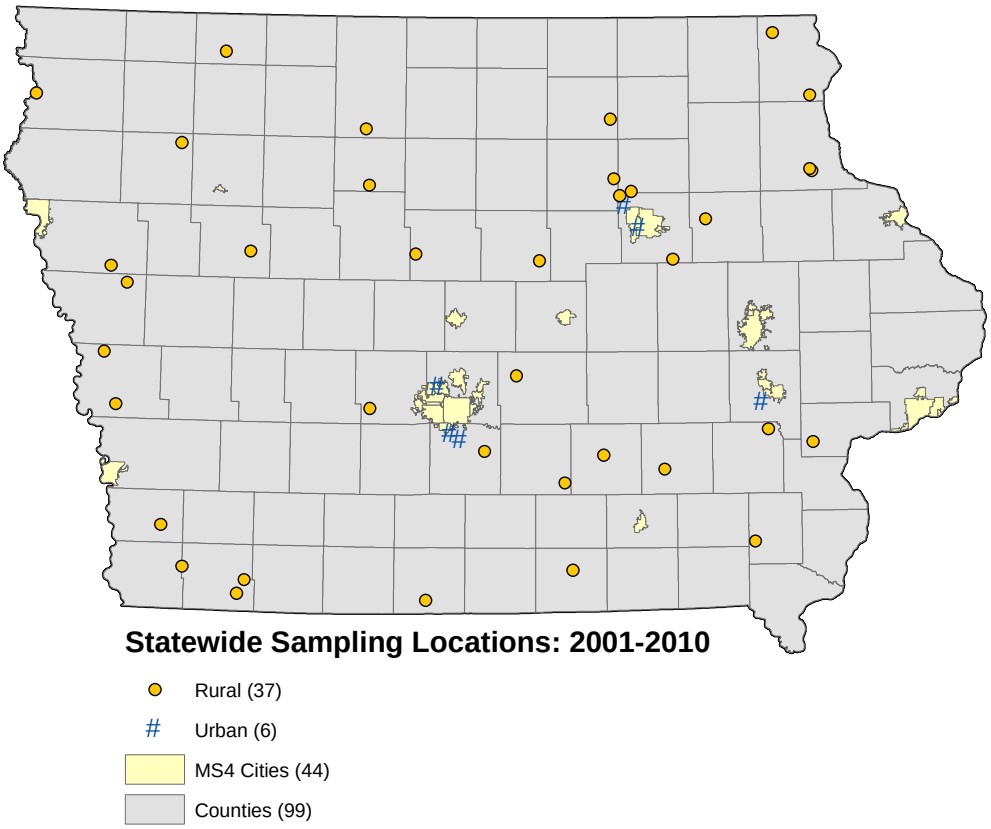

Figure 2. Final study sites based on urban and rural classifications.

3 METHODOLOGY

The null hypothesis was no trend exists in statewide data for chloride or corrosiveness indexes. This was tested using comparative statistical trend analysis. A positive trend for chloride levels in statewide water bodies would suggest an increase in concern for freshwater salinization. Depending on the corrosiveness index, positive or negative trends may also indicate an increase in large-scale environmental degradation.

3.1 Parameter Selection

The initial objective of the study was to compare chloride, corrosiveness and concentrations of zinc and copper ions across multiple sites. The ten-year dataset from 2001-2010 did include total metals sampling. However, concentrations for total copper and zinc during the 2001-2010 time series were consistently below detection level, therefore metal concentrations for this period were not included in the study. Beginning in 2016, Iowa DNR modified sampling methodologies to include low-level laboratory analysis. This modified protocol detects metals both at smaller concentrations, in micrograms per liter instead of milligrams, but also relies on a more sensitive detection method (State Hygienic Laboratory at the University of Iowa 1996). For the sake of comparing chloride concentrations to copper and zinc, data from the 2017-2018

sampling seasons were used, resulting in a reduced sample size of 253 for rural sites and 42 for urban sites. Because no metal concentrations from 2001 to 2010 were at or above detection level to enable statistically significant analysis, low-level metals data from 2016-2018 at the same locations were compared with corrosiveness calculations.

3.2 Corrosiveness Indexes

A series of indexes were calculated using values associated with each study site: 1) The Chloride-Sulfate Mass Ratio (CSMR), 2) Larson-Sköld corrosiveness ratio (LSCR) and the 3) Langelier Saturation Index (LSI) each generate values to determine potential for metal leaching in water. Each metric is used by the drinking water industry to determine safety of public resources for drinking water. CSMR is a basic indication of galvanic corrosion. LSCR measures the potential for lead leaching out of drinking water pipes, and LSI estimates the potential for both metal leaching and possible sequestration by carbonate ions present in water. Methods included in this study are based on USGS methodologies which calculated corrosiveness indices as a means of assessing threats to drinking water supplies on a national scale (Stets et al. 2017; Belitz et al. 2016).

3.2.1 Chloride-Sulfate Mass Ratio

The Chloride-Sulfate Mass Ratio (CSMR) is a measurement used by drinking water facilities to estimate potential for galvanic corrosion of leaded connections in the distribution system (Nguyen et al. 2011). The ratio uses chloride and sulfate measurements in milligrams per liter (mg/L).

Nguyen and others developed a three-tiered method for water utilities to determine appropriate treatment to avoid galvanic corrosion of lead (Belitz et al. 2016; Nguyen et al. 2011). This decision-making hierarchy compares CSMR values and alkalinity, using concentrations in milligrams per liter to determine the potential to promote galvanic corrosion (PPGC). See Table 1 for interpretation. If alkalinity is low and CSMR values are low, potential for galvanic corrosion is also low. If alkalinity is high, and CSMR values are between 0.2 and 0.5, there is moderate potential for corrosion. If alkalinity is low, and CSMR values are high, galvanic corrosion is likely.

Table 1. CSMR index value interpretation.

CSMR Value	Alkalinity (CaCO3 in mg/L)	PPGC
< 0.20	<50	Low
0.20 to 0.50	>50	Moderate
>0.50	< 50	High

3.2.2 Larson Sköld Corrosiveness Ratio

The Larson Sköld Corrosiveness Ratio (LSCR) assesses the equivalent total values of chloride and sulfate in comparison to bicarbonate measured as alkalinity (Larson and Skold 1958; Schock and Lytle 2011). Like CSMR, LSCR determines potential for lead leachate from solder used in pipe fitting, lead and brass materials (galvanic corrosion). Values > 0.6 indicate potential lead leachate from pipes (Stets et al. 2017). The LSCR applies concentrations of chloride, sulfate, and alkalinity as bicarbonate in milligrams per liter, respectively. Concentrations were converted to equivalents by dividing by

molar mass and multiplied by valence charge to calculate the ratio based on the formula below, where *x is*:

(1)

$$\frac{\left(\frac{Cl^-}{35.5}\right) + \left(2x\left(\frac{SO_4^{2-}}{96.06}\right)\right)}{\left(2x\frac{Alk}{100.08}\right)}$$

Whereas the CSMR estimates potential galvanic corrosion, LSCR is a molar ratio used by the water supply industry to determine the corrosiveness of water to mild steel. Corrosion is likely with values >0.5, and >1 are of greatest concern for lead leaching in water from pipes.

3.2.3 Langelier Saturation Index

The Langelier Saturation Index (LSI) estimates the potential and extent of calcium scale buildup within a water distribution system. If scale is not present, metals such as lead may dissolve in water (Langelier 1936; Stumm and Morgan 1981; Hu et al. 2015). Carbonate scaling may sequester metals present in runoff (Garrels and Christ 1965). The ratio is computed as the difference between the measured pH of the water and the pH at calcite saturation (pH_s) (Langelier 1936; Larson et al. 1942). The pH_s is computed from alkalinity as $CaCO_3$, hardness as calcium ions (Ca^{2+} as $CaCO_3$), total dissolved solids (TDS), all measured in milligrams per liter, and water temperature in degrees Celsius (Roberge 2007). The equation for *x is*:

(2)

$$x = pH_s = (9.3 + A + B) - (C + D)$$

$$A = \frac{log_{10}[TDS] - 1}{10}$$

$$B = (-13.2\ x)\ log_{10}(Temp\ in\ ℃) + 273) + 34.55$$

$$C = log_{10}[Ca^{2+}\ as\ CaCO_3] - 0.4$$

$$D = (log_{10}[Alkalinity\ as\ CaCO_3])$$

As an approximate indicator of the degree of saturation of calcium carbonate in water, an LSI value of 1 assumes equilibrium, with positive values indicating scale formation (Langelier 1936). Negative LSI values suggest a low likelihood of calcium carbonate scale formation. Values close to zero may indicate borderline conditions (Roberge 2007). See Table 2 for an interpretation of the LSI values. Calculations for this study are based on USGS methods (See Stets et al., 2017). Negative values suggest potentially corrosive water, whereas LSI values greater than 0.5 are considered scale forming, thus likely sequestering metals in carbonate deposition (Langland and Dugas 1996; Belitz et al. 2016). Should more corrosive water mobilize metals, the presence of

carbonate ions may actually sequester the material via lime scale, thus reducing effects via chemical reaction.

Table 2. LSI index value interpretation.

LSI Value	Corrosion Potential
>-0.50	Potentially Corrosive
-0.5. to 0.50	Indeterminate
>0.50	Scale Forming
1	Equilibrium

3.3 Surrogate data

Alkalinity measurements were unavailable for the 10-year public dataset due to agency data gaps. Two values for alkalinity were used to determine "best case" and "worst case" scenarios. An average alkalinity of 210 mg/L based on values from all available statewide sample data from the Iowa DNR Ambient Monitoring Program during the 2001-2010 study period. This value was estimated as a "best case scenario" concentration, however it does not take into account seasonal and site-specific variability typically associated with alkalinity. Lower alkalinity has been detected in urban runoff samples in the Midwest (Masterson and Bannerman 1994). This reduced alkalinity is likely attributed to surface-driven hydrology and lack of carbonate ions sourced to groundwater. As a result, an alkalinity of 79.2 mg/L was chosen to represent "worst case" scenario conditions for index calculations.

When calculating ionic strength and ion balances, direct measures of total hardness were used as a surrogate for alkalinity. Total hardness is often approximately equal to this value, especially in regions dominated by limestone geology areas, as calcium carbonate undergoes chemical weathering with weak acid from the atmosphere (H_2CO_3) to form both hardness and alkalinity in a 1:1 equivalency ratio (Schnoor, personal communication). Because of ion exchange in natural waters, two equivalents of hardness and two equivalents of alkalinity (bicarbonate alkalinity) are produced in the solution. Road maintenance activity within the study area was assumed to consist only of sodium chloride applications. If salting involves calcium nitrate or calcium chloride, the two equivalents are not produced because calcium hardness is created by the road salt itself and zero alkalinity is produced.

3.4 Trend Analysis

As a *de facto* method of trend detection in water quality data, the Mann-Kendall statistic was applied to median and maximum ionic strength and to chloride zinc, copper, and index concentrations to assess directionality and magnitude of ten-year trends in concentration. The Mann-Kendall statistic is an alternative to simple linear regression to detect monotonic trends in data collected over a time series with serial correlation. The test was selected for this study due to the small sample size, and because data were collected in a monthly time series over a ten-year period. The test assumes no serial correlation over time; representative samples are free from bias, and any monotonic trends present are directional (positive or negative). The null hypothesis assumed no trend occurs regardless of location. Should a significant trend exist, the Sen Slope Estimator determines the direction and magnitude.

Nonparametric statistics were calculated using SPSS™ statistical software and plotted in Microsoft® Excel™. The nonparametric Mann–Whitney *U* test was applied to compare median and maximum concentrations of chloride, zinc, copper and ionic strength based on location and data source. A series of corrosiveness index values were calculated for each site based on median and maximum values of each parameter. Temporal trends in chloride concentration and index values were calculated and compared by location based on median and maximum values. The Mann–Whitney *U* test was also run for data based on percentage of impervious cover within a 5-mile radius of the HUC-12 watershed area associated with each sampling location (Yin et al. 2005).

The Man-Whitney *U* test compares differences between two independent groups of continuous variables that assume a non-normal frequency distribution. The unbiased *U* statistic is a function of the cumulative probability distribution based on the population median as the measure of central tendency. The test does not require normally distributed data and can verify whether independent samples were selected from populations having the same distribution. The statistic can be used to compare data collected from different locations (Cooper et al. 2014). This test relies upon median values, which have been considered better measures of central tendency for water quality data than using the mean and a standard *t* test.

4 RESULTS AND DISCUSSION

4.1 Summary

The 2001-2010 data set has no statistically significant difference in chloride concentrations for sites in proximity to MS4 cities in comparison to sites located in more rural areas. At the statewide scale, no detectable differences appear for sites closer to MS4 cities. In fact, statewide trend analysis indicates chloride concentrations to be decreasing over time. Similarly, corrosiveness indexes indicate little cause for concern in statewide data, possibly due to overall increases in baseflow and the geology of local water systems. There appears, however, to be potential for galvanic corrosion in all sample data, regardless of urban or rural classification. 2016-2018 sample data suggest sediment present in surface water may contribute more to increased copper and zinc concentrations than corrosiveness.

4.2 Data Relationships

In nearly every instance, the values for urban locations fall within the full distribution. In all instances, chloride concentrations fall within the same distributions for both sample groups. Corrosiveness indexes for the study period rely upon surrogate data. Only one site included in the study yielded alkalinity measurements for the time period.

Table 3 includes rural sample data, depicting negative correlations between chloride and zinc (–0.245, $p<0.01$) and chloride and TSS (–0.431, $p<0.01$). No other statistically significant correlations exist in statewide data for chloride. However, TSS also weakly correlates with copper (0.213, $p<0.01$) and zinc (0.187, $p<0.01$). Copper also correlates with zinc (0.113, $p<0.05$). These results indicate sediment may play a stronger role in the presence of metals in statewide surface water measurements.

Table 3. Correlation of chloride, metals and TSS for rural sample data: 2016-2018.

		Copper	Zinc	TSS
Chloride	Correlation Coefficient	–0.004	–0.245**	–0.431**
	Sig. (2-tailed)	0.939	0.000	0.000
	N	318	318	318
Copper	Correlation Coefficient	1	0.113*	0.213**
	Sig. (2-tailed)		–0.045	0.000
	N		318	318
Zinc	Correlation Coefficient			0.187**
	Sig. (2-tailed)			0.001
	N			318

**. Correlation is significant at the 0.01 level (2-tailed).
*. Correlation is significant at the 0.05 level (2-tailed).

Results also indicate chloride does not appear to strongly influence metal concentrations in urban runoff. For urban samples, only weak, negative correlations exist between chloride, copper, zinc and TSS, as depicted in Table 4. No statistically significant correlations were detected within the data set. TSS does not appear to influence the presence of metals in urban sample data to the effect that it influences concentrations of copper and zinc from samples collected in the more rural locations. This may be due to the higher overall concentration of sediment as suspended solids in surface water near more rural locations across Iowa. Efficient drainage, impervious surfaces, and subsequent increases in flow in urban areas may also dilute runoff and surface water.

Table 4. Urban sample correlations for chloride, metals and TSS for urban sample data: 2016-2018.

		Copper	Zinc	TSS
Chloride	Correlation Coefficient	–0.044	–0.197	–0.273
	Sig. (2-tailed)	0.757	0.165	0.052
	N	51	51	51
Copper	Correlation Coefficient		0.086	–0.021
	Sig. (2-tailed)		0.550	0.886
	N		51	51
Zinc	Correlation Coefficient			0.204
	Sig. (2-tailed)			0.151
	N			51

4.3 Nonparametric Comparison of Urban and Rural Data Distributions

When considering statewide data from 2016-2018, which includes metal sampling, no significant difference appears between urban and rural categories of sample locations. The nonparametric Mann–Whitney test was applied to compare median and maximum

concentrations of chloride and index calculations based on urban and rural category types. See
Table 5 for a display of test results. Because no statistically significant difference in median values or data distributions exist for chloride concentrations, all tests for index calculations fail to reject null hypothesis of equal values and or distributions.

When comparing urban and rural sites overall, no significant difference results from the Mann-Whitney test. All values suggest a failure to reject the null hypothesis that values from urban and rural sites are from the same population.

Table 5 displays all test statistics and indicate any sample may likely occur within either category despite the magnitude or direction of trend. Also, results for all test statistics are negative, with only the Z statistic for copper (–0.139) indicating a distribution within one standard deviation of the anticipated value. All other values are at least one deviation below the expected mean, and chloride concentrations are more than two standard deviations below, $p = 0.035$. This large, negative value may reflect the declining trend in chloride concentrations in both rural and urban sample data but does not indicate a difference between samples collected from either category.

Table 5. Mann-Whitney test statistics for comparing urban and rural site data: 2016-2018.

	Chloride	Copper	Zinc	TSS
Mann-Whitney U	6,616.5	8,010.5	7,143.5	7,399
Wilcoxon W	57,337.5	58,731.5	57,864.5	8,725
Z	–2.113	–0.139	–1.366	–1.005
Asymp. Sig. (2-tailed)	0.035	0.889	0.172	0.315

4.4 Potential for Corrosion, Metal Leaching

Initial index calculations for the ten-year dataset indicate potential for galvanic corrosion in all samples, regardless of urban or rural classification. Potential corrosion, as indicated by the Larson-Sköld Index, suggest greater potential for steel and iron corrosion in rural areas, particularly when computing the index using maximum values. In nearly all instances, for the likelihood of scale formation based on LSI values indicate any mobilized metal ions will likely bond to calcium deposits. In the case of infrastructure adjacent to rural waters, this may include calcium buildup in storm sewers, or other constructed drainage networks.

Figure 3 depicts disparity between urban maximum (yellow bars) and rural maximum (orange bars) CSMR values. Index values are based on respective parameter values for median and maximum chloride concentrations. Because sulfate is likely influencing conditions more than chloride, lower CSMR index values occur when chloride concentrations are at their highest. Such is the case for both urban and rural sites. Meanwhile, median values for urban and rural CSMR values appear more similar, depicted by the blue and gray bars. The red bar signifies a threshold index value of 0.5 as potential to promote galvanic corrosion. Impervious surfaces may likely introduce more surface-water runoff, influencing the proportion of groundwater to freshwater in urban locations. Both urban median and maximum CSMR values tend to suggest potential for galvanic corrosion, as does the rural median index value for most years. However, when considering conditions in rural areas where maximum chloride values occur, it appears other values, including sulfate, are also likely present in higher

concentrations. This reduces the CSMR value for rural maximum chloride conditions and indicates lower potential for galvanic corrosion when these conditions occur.

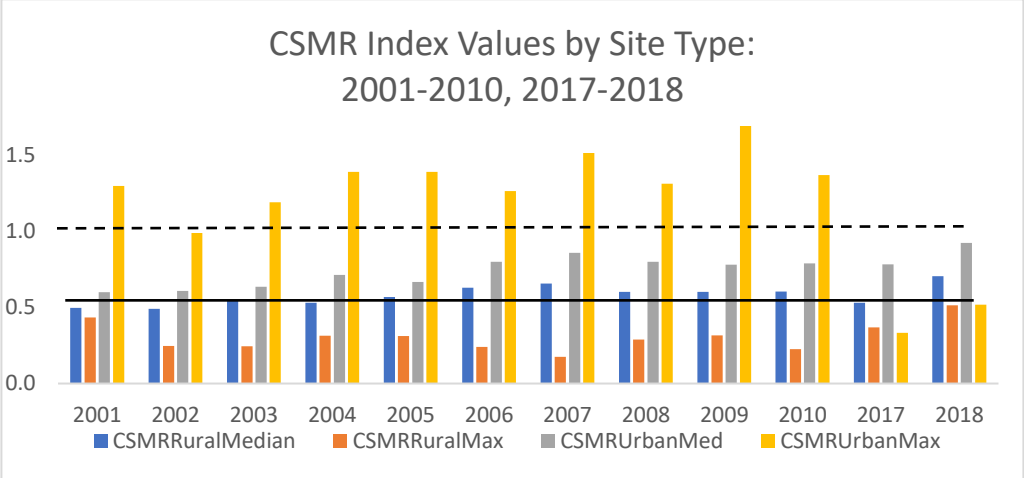

Figure 3. CSMR Values for urban and rural sites under median and maximum Cl conditions for the periods 2001-2010 and 2017-2018, and potential for galvanic corrosion indicated in red.

When alkalinity is incorporated as a value measuring corrosiveness, concern decreases. Figure 4 displays Larson-Sköld index values for median and maximum values. In this instance, maximum index values for rural sites (orange bar) appear higher than all other values. Urban maximum values (yellow bar) also appear higher overall than median urban and rural index values (blue and gray bars). Corrosion is likely with values >1 are of greatest concern as indicated by the dashed horizontal line, and all maximum index values for both urban and rural locations exceed 0.5, as indicated by the solid horizontal line.

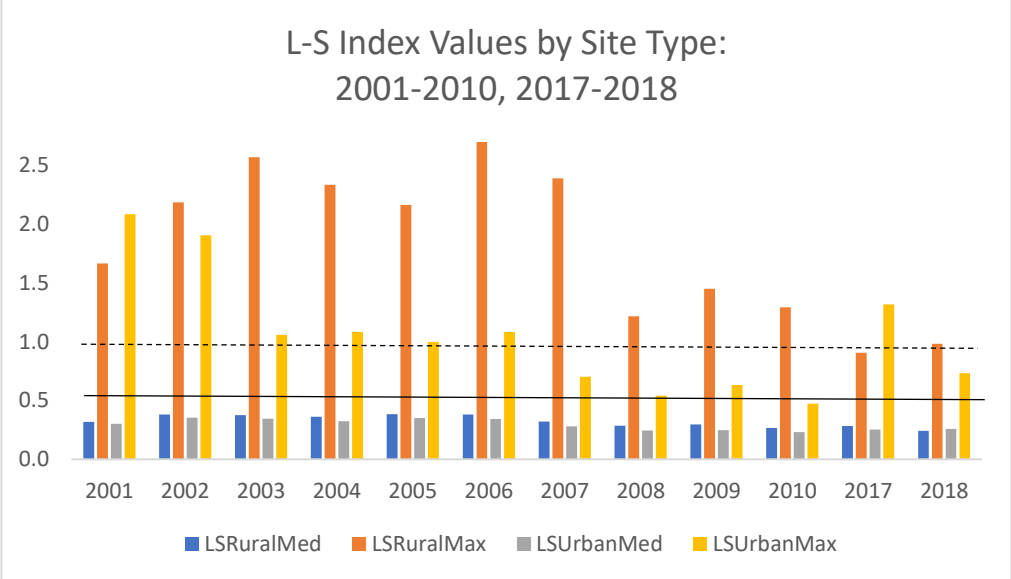

Figure 4. Larson-Sköld Index values for urban and rural locations for the period 2001-2010 and 2017-2018, and potential for lead leaching beginning to occur in the solid line at 0.5 and likely to occur in the dashed line at 1.0.

Saturation index values indicate, in most instances, scale formation sequesters mobile ions in both urban and rural areas. Langelier Saturation Index values greater than 0.5 are considered scale forming, thus likely sequestering metals in carbonate deposition. In all locations, median and maximum index values exceed 0.5, as also indicated by the solid line in Figure 5. A high concentration of groundwater in larger river systems likely sequesters any mobilized ions. This may apply in streams where groundwater maintains base flow. However, urban streams with surface-water hydrology may experience different conditions.

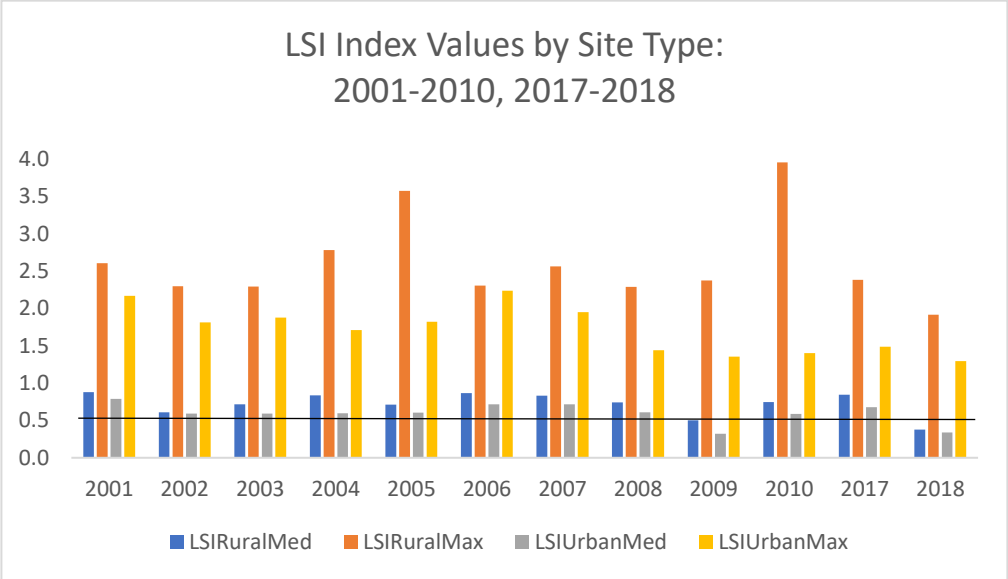

Figure 5. LSI calculations for 2001-2010, 2017-2018 median and maximum values, and potential for scale formation at 0.5, indicated by the horizontal line.

The two-year sample set reflects similar conditions of the ten-year set in terms of CSMR values for urban and rural sites. In most instances, there is a high potential for galvanic corrosion regardless of location, as CSMR values exceed 0.5. Tendencies for steel and iron corrosion as indicated by LSI values are also moderate to high. However, for the two-year dataset, urban sites indicate the greatest potential for concern. Data from 2018 sampling at both urban and rural locations suggest an indeterminate level of potential scale formation, whereas 2017 data are similar to the ten-year dataset, suggesting high potential for scale buildup, and potential metal sequestration.

When considering maximum values, most metals released are likely sequestered by calcium deposition in both urban and rural locations, with higher concentrations of zinc than copper in both site categories. Maximum CSMR values are comparable to median values, whereas LS and LSI maximum values occur above 1 for both urban and rural locations, indicating a likelihood of metal sequestration. Therefore, if more metals are released in waters measured at this scale, it is likely that the mobilized ions will then be sequestered due to the high volume of groundwater present in receiving streams.

4.5 Monotonic Trend Detection

Of all indexes and trend analyses calculated for the ten-year dataset, only median CSMR values are increasing over time, for all Iowa sites. All other trends are either declining or non-detectable. (See Table 6). Larson-Sköld Index values, while declining, remain relatively high. Maximum annual index values for the 2001-2010 were typically greater than 0.5 and in many instances were also greater than 1.0.

Table 6. Summary table of Mann-Kendall trend analysis of 10-year data (2001-2010) and corresponding figure letters for significant trends.

Parameter	Type	Mann-Kendall Trend Detection		Figure Letter
		Median	Maximum	
Chloride	Rural	No Trend	No Trend	
	Urban	Decreasing (sig p<0.05)	Decreasing (sig p<0.05)	A, B
CSMR	Rural	Increasing (sig p<0.05)	No Trend	C
	Urban	Increasing (sig p<0.05)	No Trend	D
Larson-Sköld Index	Rural	No Trend	No Trend	
	Urban	No Trend	Decreasing (sig p<0.05)	E
Langelier Saturation Index	Rural	No Trend	No Trend	
	Urban	No Trend	No Trend	

Graphical depictions of the statistically significant trends are listed A through E in Figure 6. Letter A depicts a declining trend in median chloride concentrations for sites categorized as urban in the study. An R^2 value of 0.4665 indicates a relatively weak trend overall, and the Sen's test statistic (Z) of –2.07 indicates a significant declining trend (p<0.05*)*. Maximum chloride concentrations measured at urban locations appear to decline over time in Letter B, with a R^2 value of 0.7352 and Sen's test statistic (Z) of -3.22 (p<0.01). An assumption, with no local data to compare to trends detected from statewide samples, would be that in general chloride concentrations are decreasing in Iowa's urban watersheds.

When considering corrosiveness and statewide trends, the opposite effect appears to occur. Both urban and rural median values for the Chloride-Sulfate Mass Ratio (CSMR) indicate an increasing potential to promote galvanic corrosion (PPGC) in surface waters for Letter. Letter C depicts a relatively robust trend line for median index values for rural sample sites (R^2 = 0.6704). The Sen slope regression test statistic Z of 2.50 also indicates a robust, increasing trend (p<0.05*)*. Galvanic corrosion potential appears to be increasing over time in rural areas, relatively rapidly. Urban sites indicate a similar trend, as depicted by letter D in Figure 7, with a robust trend line R^2 value of 0.726, and a statistically significant Sen slope Z statistic of 2.33 (p<0.05*)*. When considering the origins of both urban and rural CSMR index values, median values begin on the trend line already above 0.05. This indicates that even with a ten-year increase in PPGC, values were already elevated beyond initial potential at all locations. Statewide, the potential for galvanic corrosion appears to be increasing relatively rapidly regardless of location.

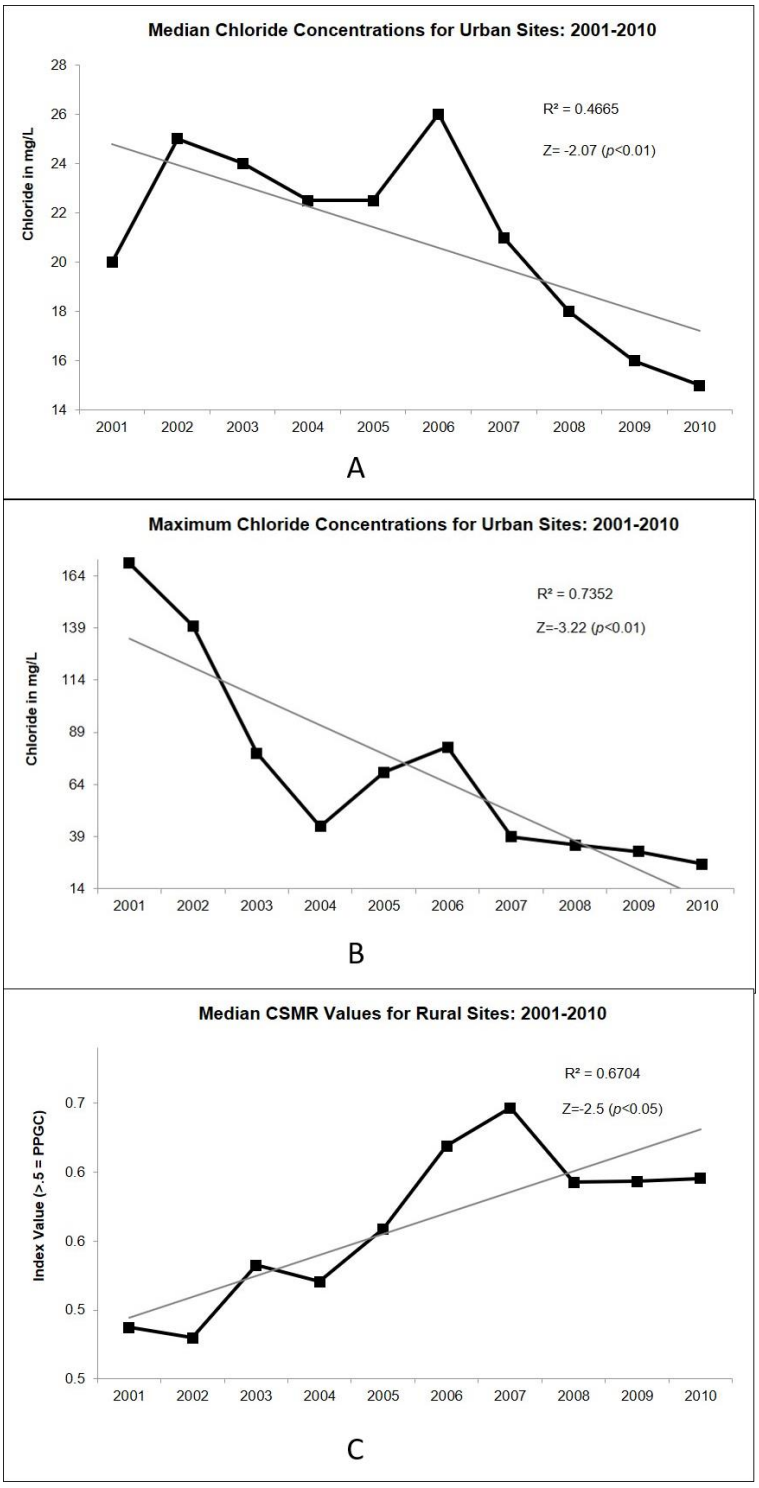

Figure 6. Trends lines corresponding with statistically significant results depicted in Table 6, Figure Letters A to C.

However, when alkalinity is taken into consideration, such as in the Larson-Sköld Index, trends indicate a decline in potential lead leaching. The only statistically significant trend detected in the ten-year data set for LSCR values occurred for index values occurring for maximum L-S index values over time in urban locations. A negative, robust trend line R^2 value of 0.8241, and a statistically significant Sen slope Z statistic of –3.22 ($p<0.05$), as indicated in Letter E.

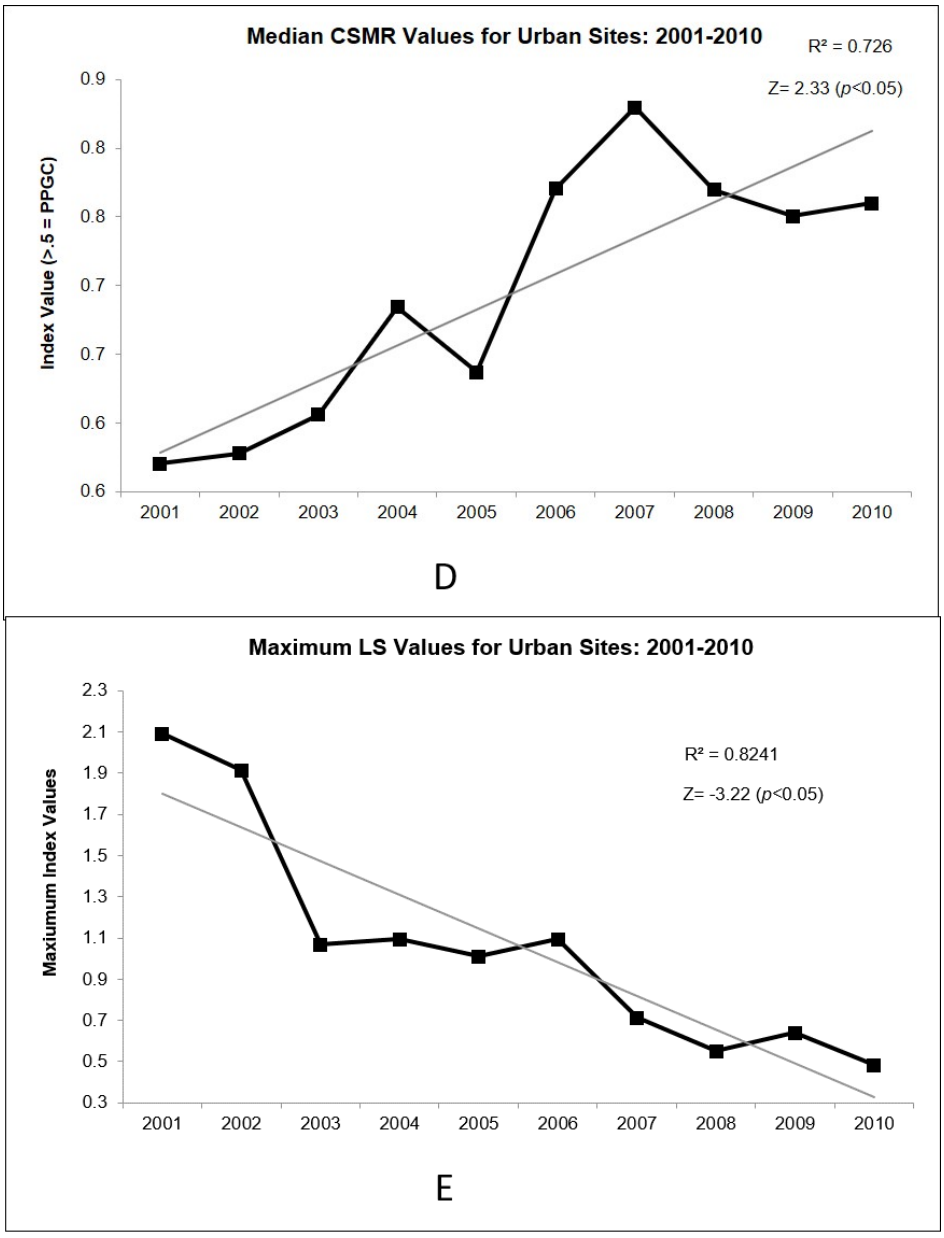

Figure 7. Trends lines corresponding with statistically significant results depicted in Table 6, Figure Letters D to E.

4.6 Discussion

While year-round chloride concentrations may not appear to increase over time in Iowa, seasonal fluctuations may still occur. Analysis of only cold season concentrations may generate different results, which serve as a subsequent study stemming from this research. Sulfate concentrations in Iowa appear to decrease over time, as indicated by both the CSMR trend and direct measurements of sulfate. When comparing chloride, sulfate and flow as discharge trends over the 2001-2010 study period, urban median chloride, sulfate and discharge appear to have inverse relationships, as depicted in Table 7. Results indicate decreasing Sen slope values of -2.07 and 2.59 and an increasing slope of 2.8 for discharge ($p>0.05$ for all). Discharge trends appear increasing for median rural measurements, with a value of 1.88 ($p>0.05$), but only declining trends for sulfate and not chloride. For median sulfate measurements at rural sites, the slope value is -2.86 ($p>0.05$).

Table 7. Chloride, sulfate, and discharge trends for site data: 2001-2010

Classifications	Sen Slope for Parameters ($p<0.05$)		
	Chloride	Sulfate	Discharge
Urban			
Median	–2.07	–2.59	2.68
Maximum	–3.22	–0.89	No trend, variable
Rural			
Median	No Trend	–2.86	1.88
Maximum	No Trend	–3.04	No trend, but increasing

No detectable trend exists when considering maximum discharges for either rural or urban sites. However, urban sites express a higher variability, and rural sites visually indicate an increase over time, despite no statistically detectable trend in urban (A) or rural (B) maximum flows cubic feet per second (CFS). See Figure 8. Should corrosiveness indexes be considered a means of assessing freshwater salinization, statewide water monitoring efforts need to include the appropriate parameters and not rely on surrogate data for calculations.

Urban runoff is more corrosive than rural runoff. Increased statewide base flows dilute chloride concentrations over time and space but may eventually increase corrosiveness over time. However, increased urban runoff from impervious surfaces do not typically mix with groundwater in stormwater infrastructure. This “carbonate-free” water cannot sequester mobile ions the way groundwater can. Urban runoff, especially from transportation surfaces, is significantly more corrosive than groundwater, and likely damages urban infrastructure to a great extent (Kauten 2020). Drainage improvements and added imperviousness reduce the overall ratio of groundwater to surface water in Iowa larger order streams. Meanwhile small, urban streams are likely increasing in corrosiveness without dilution from groundwater. Current trends indicate a decline in L-S and LSI corrosiveness index values on a statewide scale. But a progressive imbalance of groundwater to surface water may also alter chemistry on this broader scale over time. Further research might explore changes in groundwater/freshwater ratios in Iowa streams.

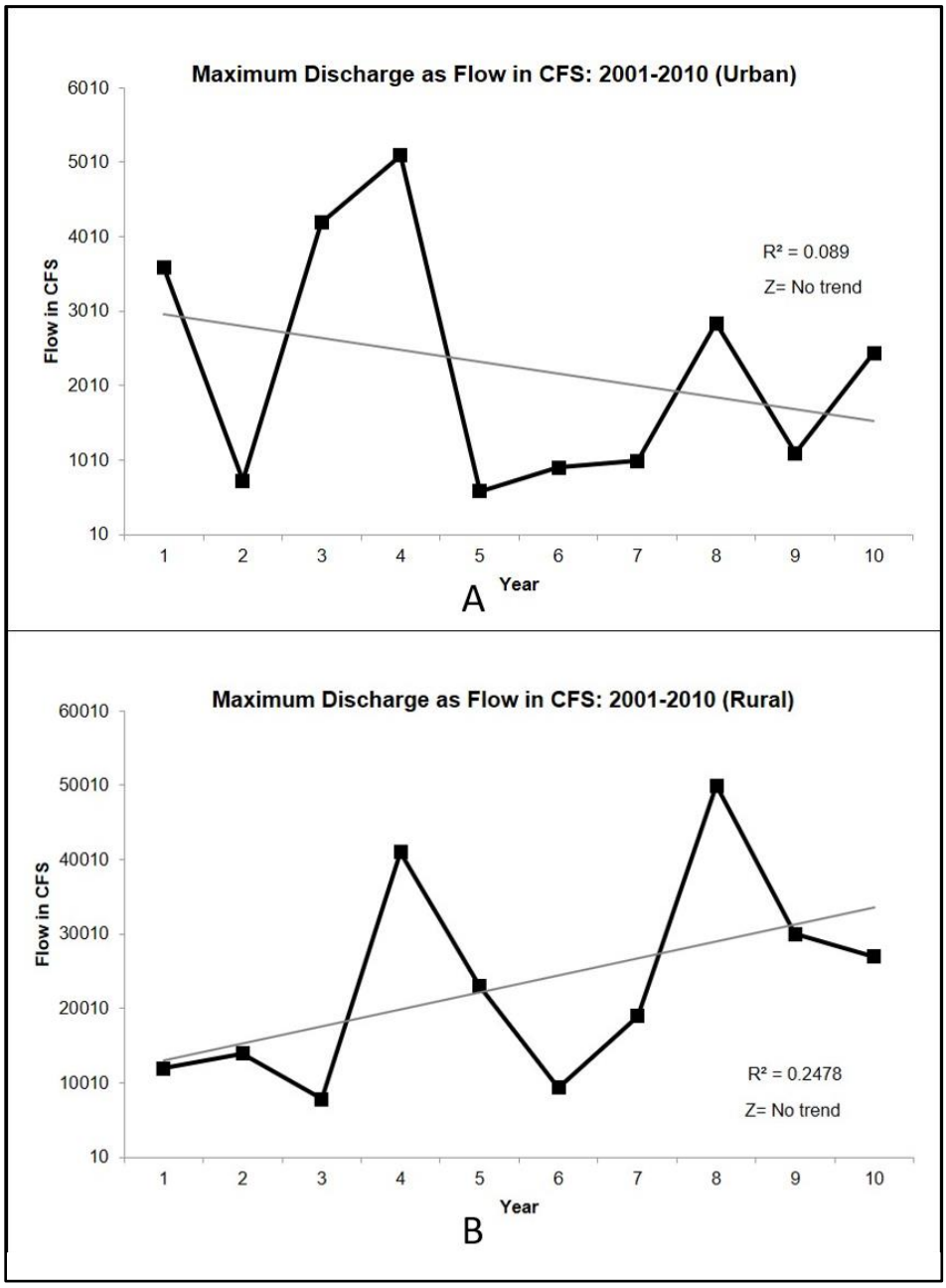

Figure 8. Trend lines for maximum discharge as flow for urban (A) and rural (B) sites.

Regardless of whether metals mobilize, local freshwater systems likely suffer from salts present in runoff, including acute and chronic biological impacts. (Boyd et al. 2016; Van Meter et al. 2011; Wallace et al. 2013). Extremely large pulses of chloride exceeding 5,000 or 6,000 mg/L, even if brief in nature, can kill macroinvertebrates and other freshwater organisms or alter biological activity over time (Kauten, 2020).

5 CONCLUSION

Statewide monitoring data indicate a decline in chloride concentrations from 2000-2010 for both urban and rural sites, but this may not suggest freshwater salinization is not occurring at all. Increases in flow regimes and a lack of consistent data collection may mask past and present conditions. Data paucity and a lack of urban monitoring sites limit the capacity of understanding urban water quality in Iowa. The fact that increasing CSMR trends is detectable at such a coarse scale likely indicates local conditions may be even worse. Should urban chloride concentrations remain unchecked, ion balances may shift away from equilibrium to the point where "hard water" longer sequesters mobile metal ions.

Assuming conditions are representative of most urban areas, it is likely that chloride concentrations are similar in most cold-climate cities. If collection methods for statewide freshwater salinity detection remain static, irreversible environmental damage is not only occurring, but remains undetected. Areas concerned about freshwater salinization should consider localized data collection to compare with statewide data and grow understanding of location conditions. Communities may also consider corrosiveness indexes as a risk assessment metric. Sole reliance on statewide data likely perpetuate a false sense of confidence regarding local water quality.

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